PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C11D 3/37 — A1

(11) International Publication Number: **WO 99/07813**

(43) International Publication Date: 18 February 1999 (18.02.99)

(21) International Application Number: PCT/US98/16495

(22) International Filing Date: 7 August 1998 (07.08.98)

(30) Priority Data:
60/055,152 8 August 1997 (08.08.97) US

(71) Applicant *(for all designated States except US)*: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: RANDALL, Sherri, Lynn [US/US]; 6841 Stone Valley Court, Hamilton, OH 45011 (US). PANANDIKER, Rejan, Keshav [US/US]; 6484 Oregon Pass, West Chester, OH 45069 (US). GOSSELINK, Eugene, Paul [US/US]; 3754 Susanna Drive, Cincinnati, OH 45251 (US). MOHR, Bernhard [DE/DE]; Obere Seegasse 12, D–69124 Heidelberg (DE). LUIPOLD, Lee, Ann [US/US]; 3121 Westbourne Drive, Cincinnati, OH 45248 (US). BOECKH, Dieter [DE/DE]; Zeppelinweg 3, D–67117 Limburgerhof (DE). NORENBERG, Ralf [DE/DE]; P.O. Box 67056, D–67056 Ludwigshafen (DE).

(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).

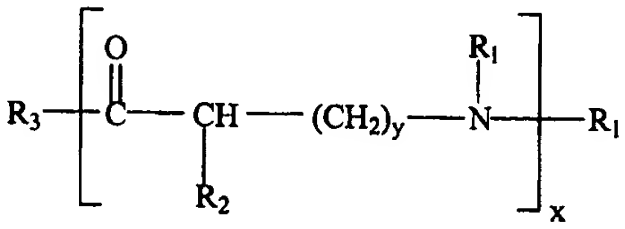
(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: LAUNDRY DETERGENT COMPOSITIONS WITH AMINO ACID BASED POLYMERS TO PROVIDE APPEARANCE AND INTEGRITY BENEFITS TO FABRICS LAUNDERED THEREWITH

(57) **Abstract**

Compositions that contain from about 1 % to about 80 % by weight of surfactants selected from the group consisting of nonionic, anionic, cationic, amphoteric, or zwitterionic surfactants, or mixtures thereof; and from about 0.1 % to about 10 %, by weight of a mixture of amino acid based polymers, oligomers or copolymers of general



(I)

formula (I) wherein the polymer, oligomer, or copolymer contains at least about 5 mole %, of one or more amino acids and an organic acid. These of amino acid based polymers, oligomers or copolymers can be obtained by condensing a basic amino acid, such as lysine, with an organic acid. The amino acid based polymer, oligomer or copolymer materials are useful as fabric treatment agents as they can impart fabric appearance and integrity benefits to fabrics and textiles laundered in washing solutions which contain such materials.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

LAUNDRY DETERGENT COMPOSITIONS WITH AMINO ACID BASED POLYMERS TO PROVIDE APPEARANCE AND INTEGRITY BENEFITS TO FABRICS LAUNDERED THEREWITH

TECHNICAL FIELD

The present invention relates to compositions, in either liquid or granular form, for use in laundry applications, wherein the compositions comprise certain amino acid based polymer, oligomer or copolymer materials which impart appearance and integrity benefits to fabrics and textiles laundered in washing solutions formed from such compositions.

BACKGROUND OF THE INVENTION

It is, of course, well known that alternating cycles of using and laundering fabrics and textiles, such as articles of worn clothing and apparel, will inevitably adversely affect the appearance and integrity of the fabric and textile items so used and laundered. Fabrics and textiles simply wear out over time and with use. Laundering of fabrics and textiles is necessary to remove soils and stains which accumulate therein and thereon during ordinary use. However, the laundering operation itself, over many cycles, can accentuate and contribute to the deterioration of the integrity and the appearance of such fabrics and textiles.

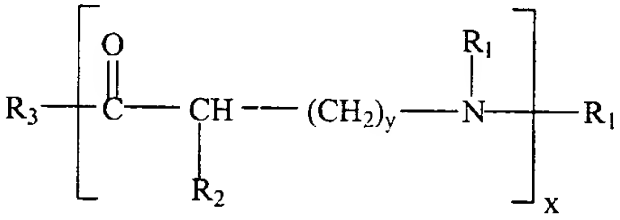
Deterioration of fabric integrity and appearance can manifest itself in several ways. Short fibers are dislodged from woven and knit fabric/textile structures by the mechanical action of laundering. These dislodged fibers may form lint, fuzz or "pills" which are visible on the surface of fabrics and diminish the appearance of newness of the fabric. Further, repeated laundering of fabrics and textiles, especially with bleach-containing laundry products, can remove dye from fabrics and textiles and impart a faded, worn out appearance as a result of diminished color intensity, and in many cases, as a result of changes in hues or shades of color.

Given the foregoing, there is clearly an ongoing need to identify materials which could be added to laundry detergent products that would associate themselves with the fibers of the fabrics and textiles laundered using such detergent products and thereby reduce or minimize the tendency of the laundered fabric/textiles to deteriorate in appearance. Any such detergent product additive material should, of course, be able to benefit fabric appearance and integrity without unduly interfering with the ability of the

laundry detergent to perform its fabric cleaning function. The present invention is directed to the use of amino acid based polymer, oligomer or copolymer materials in laundry applications which perform in this desired manner.

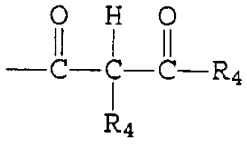
SUMMARY OF THE INVENTION

Amino acid based polymer, oligomer or copolymer materials which are suitable for use in laundry operations and provide the desired fabric appearance and integrity benefits can be characterized by the following general formula:

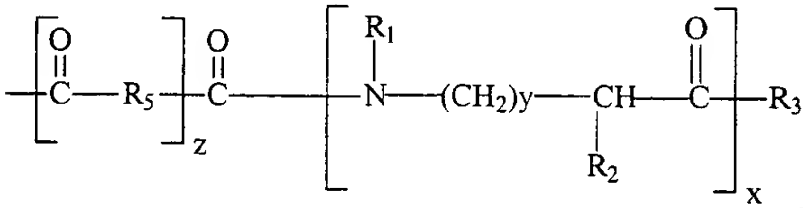


wherein the polymer, oligomer, or copolymer contains at least about 5 mole %, preferably at least about 10 mole %, more preferably from about 20 mole %, and most preferably at least about 40 mole %, of one or more basic amino acids;

each R_1 is independently selected from the group consisting of H, -C(O)-R_4, C_1-C_{18} saturated or unsaturated, branched or linear alkyl, C_2-C_{18} saturated or unsaturated, branched or linear hydroxyalkyl, C_3-C_8 cycloalkyl, C_6-C_{18} aryl, C_7-C_{18} alkylaryl, citric acid,

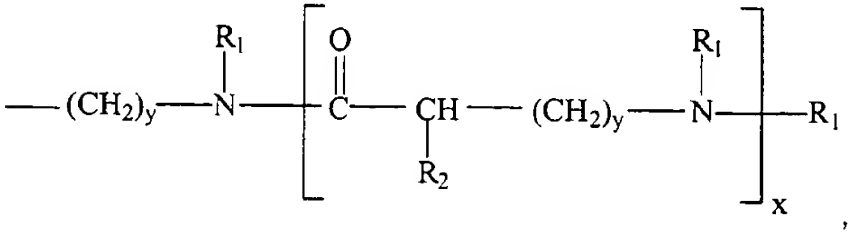


, and

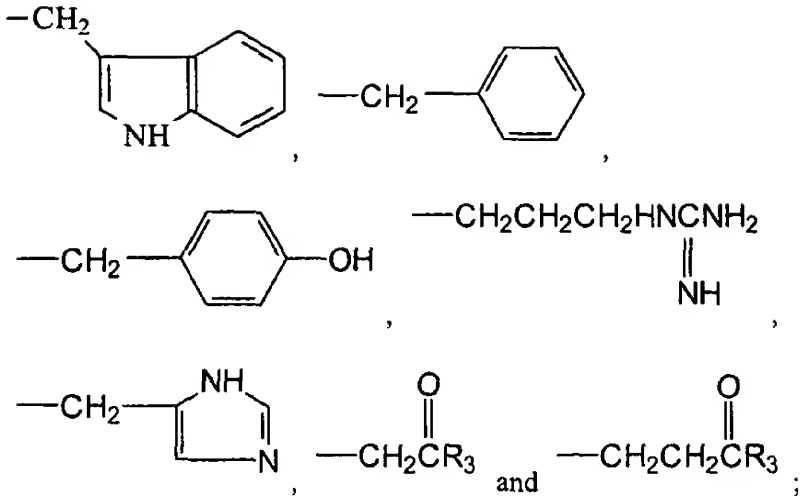


;

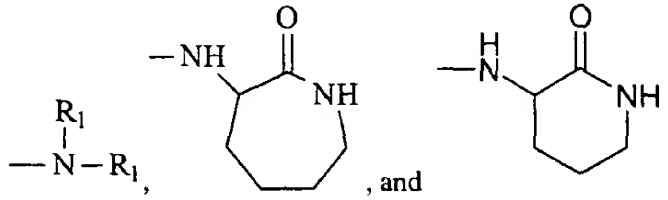
each R_2 is independently selected from the group consisting of H, NH_2,



,



each R_3 is independently selected from the group consisting of OH, OM,



;

each R_4 is independently selected from the group consisting of C_1-C_{30} saturated or unsaturated, branched or linear alkyl, C_3-C_8 cycloalkyl, C_2-C_{30} hydroxyalkyl, C_6-C_{18} aryl, C_7-C_{30} alkylaryl, and C_2-C_{100} linear or branched oxa or polyoxa-substituted alkyl;

R_5 may be absent, if R_5 is present each R_5 is independently selected from the group consisting of C_1-C_{12} linear or branched alkylene, cyclic alkylene, C_2-C_{12} linear oxa-substituted alkylene, C_2-C_{12} branched oxa-substituted alkylene, and C_3-C_{12} cyclic oxa-substituted alkylene;

wherein:

each x is independently from 0 to about 200;

each y is independently from 0 to about 10, preferably y is 0, 3 or 4, and most preferably y is 4;

each z is independently 0 or 1; and

M is selected from compatible cations; and

provided that:

- the sum of all x's is from 2 to about 200, preferably from about 3 to about 150, more preferably from about 5 to about 120, and most preferably from about 5 to about 100;

- any basic amine site on the polymer, oligomer, or copolymer may be optionally protonated, alkylated, or quaternized with constituents selected from the group consisting of H, CH_3, alkyl, hydroxyalkyl, benzyl and mixtures thereof;
- any amine site may be optionally alkoxylated; and
- when two R_1 groups are attached to a common nitrogen the two R_1s may form a cyclic structure selected from the group consisting of C_5-C_8 alkylene, and C_4-C_7 alkyleneoxyalkylene.

In one aspect of this invention there is provided a detergent composition comprising:

a) from about 1% to about 80% by weight of surfactants selected from the group consisting of nonionic, anionic, cationic, amphoteric, or zwitterionic surfactants, or mixtures thereof; and

b) from about 0.1% to about 10%, preferably from about 0.2% to about 8%, more preferably from about 0.3% to about 6%, and most preferably from about 0.4% to about 5%, by weight of a mixture of amino acid based polymers which are obtainable by condensing at a temperature of at least 120°C:

(i) a basic amino acid selected from the group consisting of lysine, arginine, ornithine, tryptophane and mixtures thereof;

(ii) a copolymerizable compound selected from the group consisting of saturated monobasic carboxylic acids, unsaturated monobasic carboxylic acids, polybasic carboxylic acids, carboxylic acid anhydrides, diketenes, monohydroxycarboxylic acids, monobasic polyhydroxycarboxylic acids and mixtures thereof; and

(iii) optionally, at least one compound selected from the group consisting of amines, lactams, nonproteinogenic acids, alcohols, alkoxylated amines, amino sugars, carbohydrates, sugar carboxylic acids and mixtures thereof; and

wherein compounds (i) and (ii) are present in a molar ratio of (i):(ii) of from 100:1 to 1:1, preferably the molar ratio of basic amino acid (i) to copolymerizable compound (ii) is of from 100:1 to 2:1, more preferably the molar ratio of basic amino acid (i) to copolymerizable compound (ii) is of from 50:1 to 2:1, and most preferably the molar ratio of basic amino acid (i) to copolymerizable compound (ii) is of from 20:1 to 5:1. The molar ratio of compounds (i):(iii) is preferably from 100:1 to 1:20.

The amino acid based polymer, oligomer or copolymer materials defined above can be used as a washing solution additive in either granular or liquid form. Alternatively, they

can be admixed to granular detergents, dissolved in liquid detergent compositions or added to a fabric softening composition. Preferably the fabric treatment compositions of this invention comprise from about 0.1% to about 10%, preferably from about 0.2% to about 8%, more preferably from about 0.3% to about 6%, and most preferably from about 0.4% to about 5%, by weight of a mixture of the amino acid based polymers, oligomers or copolymers defiened by the general formula above. The forgoing description of uses for the amino acid based fabric treatment materials defined herein are intended to be exemplary and other uses will be apparent to those skilled in the art and are intended to be within the scope of the present invention.

The laundry detergent compositions herein comprise from about 1% to 80% by weight of a detersive surfactant, from about 0.1% to 80% by weight of an organic or inorganic detergency builder and from about 0.1% to 5% by weight of the amino acid based fabric treatment materials of the present invention. The detersive surfactant and detergency builder materials can be any of those useful in conventional laundry detergent products.

Aqueous solutions of the amino acid based polymer, oligomer or copolymer materials of the subject invention comprise from about 0.1% to 50% by weight of the amino acid based fabric treatment materials dissolved in water and other ingredients such as stabilizers and pH adjusters.

In its method aspect, the present invention relates to the laundering or treating of fabrics and textiles in aqueous washing or treating solutions formed from effective amounts of the detergent compositions described herein, or formed from the individual components of such compositions. Laundering of fabrics and textiles in such washing solutions, followed by rinsing and drying, imparts fabric appearance benefits to the fabric and textile articles so treated. Such benefits can include improved overall appearance, pill/fuzz reduction, antifading, improved abrasion resistance, and/or enhanced softness.

DETAILED DESCRIPTION OF THE INVENTION

As noted, when fabric or textiles are laundered in wash solutions which comprise the amino acid based polymer, oligomer or copolymer materials of the present invention fabric appearance and integrity are enhanced. The amino acid based fabric treatment materials can be added to wash solutions by incorporating them into a detergent composition, a fabric softener or by adding them separately to the washing solution. The amino acid based fabric treatment materials are described herein primarily as liquid or granular detergent additives but the present invention is not meant to be so limited. The amino acid based fabric

treatment materials, detergent composition components, optional ingredients for such compositions and methods of using such compositions, are described in detail below. All percentages are by weight unless other specified.

A) Amino Acid Based Polymer, Oligomer or Copolymer Materials

The essential component of the compositions of the present invention comprises one or more amino acid based polymer, oligomer or copolymer. Such materials have been found to impart a number of appearance benefits to fabrics and textiles laundered in aqueous washing solutions formed from detergent compositions which contain such amino acid based fabric treatment materials. Such fabric appearance benefits can include, for example, improved overall appearance of the laundered fabrics, reduction of the formation of pills and fuzz, protection against color fading, improved abrasion resistance, etc. The amino acid based fabric treatment materials used in the compositions and methods herein can provide such fabric appearance benefits with acceptably little or no loss in cleaning performance provided by the laundry detergent compositions into which such materials are incorporated.

One preferred method for making the amino acid based polymers, oligomers or copolymers of this invention is by a condensation reaction of an amino acid and another group such as a carboxylic acid. Condensation reactions are known to those skilled in the art, and the compositions and parameters for exemplary reactions are given in the Examples below. Preferred condensates according to this invention include the condensate reaction product of lysine with at least one acid selected from the group consisting of aminocaproic acid, caprolactam, 2-ethylhexanoic acid, adipic acid, phthalic acid, terephthalic acid, oxalic acid, citric acid, C_1-C_{30} alkyldiketenes, C_1-C_{30} monocarboxylic acids that are linear or branched, saturated or unsaturated, and mixtures thereof. Preferably, the lysine and the acid are condensed at a ratio of lysine:acid of from about 1:1 to about 10:1. Additionally, lysine or other amino acids can be condensed with a combination of two or more acids selected from the group consisting of aminocaproic acid, caprolactam, 2-ethylhexanoic acid, adipic acid, phthalic acid, terephthalic acid, oxalic acid, citric acid, C_1-C_{30} alkyldiketenes, C_1-C_{30} monocarboxylic acids that are linear or branched, saturated or unsaturated, and mixtures thereof.

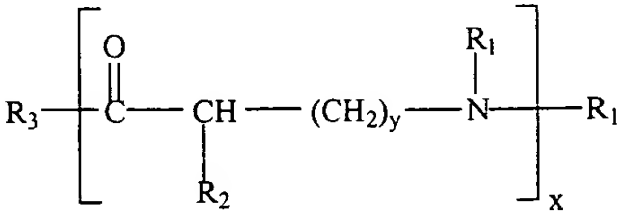
The amino acid based polymer, oligomer or copolymer component of the compositions herein may also comprise combinations of these amino acid based materials. For example, a mixture of lysine and adipic acid condensates can be combined with a

mixture of lysine and lauric acid condensates to achieve the desired fabric treatment results. Moreover, the molecular weight of amino acid based fabric treatment materials can vary within the mixture as is illustrated in Example I below.

As will be apparent to those skilled in the art, an oligomer is a molecule consisting of only a few monomer units while polymers comprise considerably more monomer units. For the present invention, oligomers are defined as molecules having an average molecular weight below about 1,000 and polymers are molecules having an average molecular weight of greater than about 1,000. Copolymers are polymers or oligomers wherein two or more dissimilar monomers have been simultaneously or sequentially polymerized. Copolymers of the present invention can include, for example, polymers or oligomers polymerized from a mixture of a primary amino acid based monomer, e.g., lysine, and a secondary amino acid monomer, e.g., tryptophan.

The amino acid based fabric treatment component of the detergent compositions herein will generally comprise from about 0.1% to about 10%, preferably from about 0.2% to about 8%, more preferably from about 0.3% to about 6%, and most preferably from about 0.4% to about 5%, by weight of a mixture of the amino acid based polymers, oligomers or copolymers defined by the general formula below. But when used as a washing solution additive, i.e. when the amino acid based fabric treatment component is not incorporated into a detergent composition, the concentration of the amino acid based component can comprise from about 0.1% to about 50% by weight of the additive material.

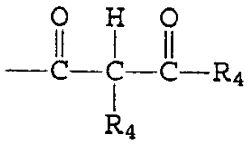
One suitable group of amino acid based polymer, oligomer or copolymer materials for use herein is characterized by the following formula:



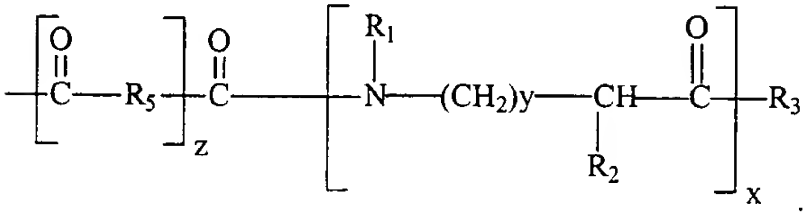
wherein the polymer, oligomer, or copolymer contains at least about 5 mole %, preferably at least about 10 mole %, more preferably from about 20 mole %, and most preferably at least about 40 mole %, of one or more basic amino acids;

each R_1 is independently selected from the group consisting of H, -C(O)-R_4,

C_1-C_{18} saturated or unsaturated, branched or linear alkyl, C_2-C_{18} saturated or unsaturated, branched or linear hydroxyalkyl, C_3-C_8 cycloalkyl, C_6-C_{18} aryl, C_7-C_{18} alkylaryl, citric acid,

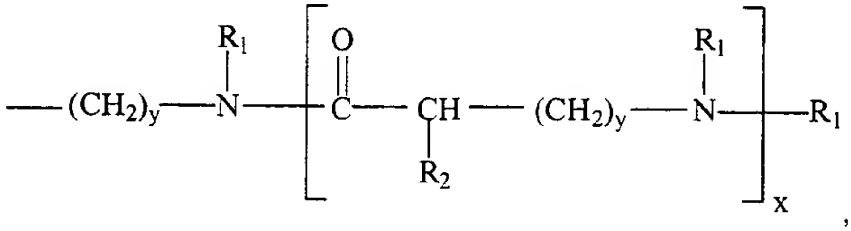


, and

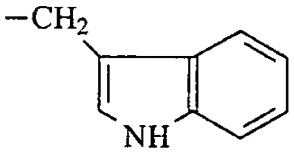


;

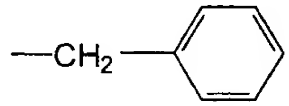
each R_2 is independently selected from the group consisting of H, NH_2,



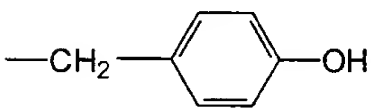
,



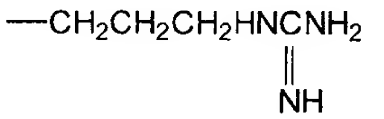
,



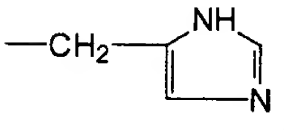
,



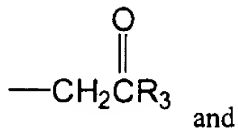
,



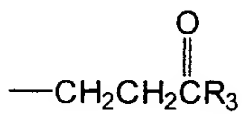
,



,

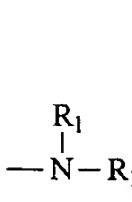


and

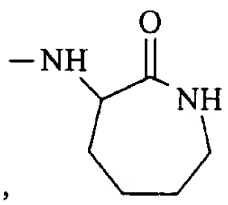


;

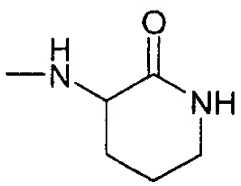
each R_3 is independently selected from the group consisting of OH, OM,



,



, and



;

each R_4 is independently selected from the group consisting of C_1-C_{30} saturated or unsaturated, branched or linear alkyl, C_3-C_8 cycloalkyl, C_2-C_{30} hydroxyalkyl, C_6-

C_{18} aryl, C_7-C_{30} alkylaryl, and C_2-C_{100} linear or branched oxa or polyoxa-substituted alkyl;

R_5 may be absent, if R_5 is present each R_5 is independently selected from the group consisting of C_1-C_{12} linear or branched alkylene, cyclic alkylene, C_2-C_{12} linear oxa-substituted alkylene, C_2-C_{12} branched oxa-substituted alkylene, and C_3-C_{12} cyclic oxa-substituted alkylene;

wherein:

each x is independently from 0 to about 200;

each y is independently from 0 to about 10;

each z is independently 0 or 1; and

M is selected from compatible cations; and

provided that:

- the sum of all x's is from 2 to about 200, preferably from about 3 to about 150, more preferably from about 5 to about 120, and most preferably from about 5 to about 100;
- any basic amine site on the polymer, oligomer, or copolymer may be optionally protonated, alkylated, or quaternized with constituents selected from the group consisting of H, CH_3, alkyl, hydroxyalkyl, benzyl and mixtures thereof;
- any amine site may be optionally alkoxylated; and
- when two R_1 groups are attached to a common nitrogen the two R_1s may form a cyclic structure selected from the group consisting of C_5-C_8 alkylene, and C_4-C_7 alkyleneoxyalkylene.

Preferably, no nitrogen in the structure defined above has more then one acyl group directly attached to it.By "basic" amino acid it is intended that the amino acid should have a reactive nitrogen cite after polymerization. Basic amino acids include lysine, arginine, histidine, tryptophane and orinthine.

In one aspect of this invention there is provided a detergent composition comprising:

a) from about 1% to about 80% by weight of surfactants selected from the group consisting of nonionic, anionic, cationic, amphoteric, or zwitterionic surfactants, or mixtures thereof; and

b) from about 0.1% to about 10%, preferably from about 0.2% to about 8%, more preferably from about 0.3% to about 6%, and most preferably from about 0.4%

to about 5%, by weight of a mixture of amino acid based polymers which are obtainable by condensing at a temperature of at least 120°C:

(i) a basic amino acid selected from the group consisting of lysine, arginine, ornithine, tryptophane and mixtures thereof;

(ii) a copolymerizable compound selected from the group consisting of saturated monobasic carboxylic acids, unsaturated monobasic carboxylic acids, polybasic carboxylic acids, carboxylic acid anhydrides, diketenes, monohydroxycarboxylic acids, monobasic polyhydroxycarboxylic acids and mixtures thereof; and

(iii)optionally, at least one compound selected from the group consisting of amines, lactams, preferably, lactams having 5 to 13 atoms in the ring, nonproteinogenic acids, alcohols, alkoxylated amines, amino sugars, carbohydrates, sugar carboxylic acids and mixtures thereof; and

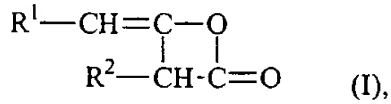
wherein compounds (i) and (ii) are present in a molar ratio of (i):(ii) of from 100:1 to 1:1, preferably the molar ratio of basic amino acid (i) to copolymerizable compound (ii) is of from 100:1 to 2:1, more preferably the molar ratio of basic amino acid (i) to copolymerizable compound (ii) is of from 50:1 to 2:1, and most preferably the molar ratio of basic amino acid (i) to copolymerizable compound (ii) is of from 20:1 to 5:1. The molar ratio of compounds (i):(iii) is preferably from 100:1 to 1:20.

Preferably the detergent compositions of this invention comprise amino acid based polymers that are obtained by condensing lysine, and at least one compound selected from the group consisting of palmitic acid, stearic acid, lauric acid, octanoic acid, propionic acid, acetic acid, 2-ethylhexanoic acid, adipic acid, succinic acid, citric acid and mixtures thereof. Even more preferably, the copolymerizable compound, (ii), comprises at least one alkyldiketene having 1 to 30 carbon atoms in the alkyl group.

More Specificaly, The copolymerizable compounds (ii) are selected from the group consisting of saturated monobasic carboxylic acids, unsaturated monobasic carboxylic acids, polybasic carboxylic acids, carboxylic acid anhydrides, diketenes, monohydroxycarboxylic acids, monobasic polyhydroxycarboxylic acids and mixtures thereof. Examples of saturated monobasic carboxylic acids are formic acid, acetic acid, propionic acid, butyric acid, valeric acid, capric acid, lauric acid, palmitic acid, stearic acid, arachidic acid, behenic acid, myristic acid, undecanoic acid, 2-ethyl hexanoic acid, and all naturally occurring fatty acids and mixtures thereof.

Examples of unsaturated monobasic carboxylic acids are acrylic acid, methacrylic acid, crotonic acid, sorbic acid, oleic acid, linoleic acid, and erucic acid. Examples of polybasic carboxylic acids are oxalic acid, fumaric acid, maleic acid, malonic acid, succinic acid, itaconic acid, adipic acid, aconitic acid, suberic acid, azeleic acid, pyridinedicarboxylic acid, furandicarboxylic acid, phthalic acid, tarephthalic acid, digylcolic acid, glutaric acid, substituted C_4-dicarboxylic acid, sulfosuccinic acid, C_1- to C_{26}-alkylsuccinic acids, C_2- to C_{26}-alkenylsuccinic acids, 1, 2, 3-propanetricarboxylic acids, 1, 1, 3, 3-propanetetracarboxylic acids, 1,1,2,2-ethanetetracarboxylic acid, 1,2,3,4-butanetetracarboxylic acid, 1,2,2,3-propanetetracarboxylic acid, 1,3,3,5-pentanetetracarboxylic acid, 1,2,4-benzenetricarboxylic acid, and 1,2,4,5-benzenetetracarboxylic acid. Polybasic carboxylic acids which can form carboxylic anhydrides are also suitable as compounds (b), for example succinic anhydride, mono and dianhydride of butanetetracarboxylic acid, phthalic anhydride, acetylcitric anhydride, maleic anhydride, itaconic anhydride, and aconitic anhydride.

Examples of diketenes which may be used as component (b) are alkyl diketenes having 1 to 30 carbon atoms. These diketenes may be characterized by the following formula:



(I),

wherein the substituents R^1 and R^2 have the same meaning or are different C_1- to C_{30}-, preferably C_6- to C_{22}-saturated or ethylenically unsaturated alkyl. Compounds of formula (I) are for example hexyl diketene, cyclohexyl diketene, octyl diketene, decyl diketene, dodecyldiketene, palmityl diketene, stearyl diketene, oleyl diketene, ocatdecyl diketene, eicosyl diketene, docosyl diketene, and behenyl diketene.

Examples of monohydroxycarboxylic acids are malic acid, tartronic acid, citric acid, and isocitric acid. Polyhydroxycarboxylic acids are for example tartaric acid, mucic acid, glyceric acid, bis (hydroxymethyl) propinonic acid, gluconic acid, and hydroxylated unsaturated fatty acids such as dihydroxystearic acid.

In the Example section below, specific condensation reaction parameters are disclosed. In light of these examples, the specific details regarding the condensation reaction of an amino acid and an organic acid will be apparent to those skilled in the art.

B) Detersive Surfactant

The detergent compositions herein comprise from about 1% to 80% by weight of a detersive surfactant. Preferably such compositions comprise from about 5% to 50% by weight of surfactant. Detersive surfactants utilized can be of the anionic, nonionic, zwitterionic, ampholytic or cationic type or can comprise compatible mixtures of these types. Detergent surfactants useful herein are described in U.S. Patent 3,664,961, Norris, issued May 23, 1972, U.S. Patent 3,919,678, Laughlin et al., issued December 30, 1975, U.S. Patent 4,222,905, Cockrell, issued September 16, 1980, and in U.S. Patent 4,239,659, Murphy, issued December 16, 1980. All of these patents are incorporated herein by reference. Of all the surfactants, anionics and nonionics are preferred.

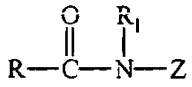
Useful anionic surfactants can themselves be of several different types. For example, water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylolammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Additional non-soap anionic surfactants which are suitable for use herein include the water-soluble salts, preferably the alkali metal, and ammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are a) the sodium, potassium and ammonium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8-C_{18} carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; b) the sodium, potassium and ammonium alkyl polyethoxylate sulfates, particularly those in which the alkyl group contains from 10 to 22, preferably from 12 to 18 carbon atoms, and wherein the polyethoxylate chain contains from 1 to 15, preferably 1 to 6 ethoxylate moieties; and c) the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Especially valuable are linear straight

chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C_{11-13} LAS.

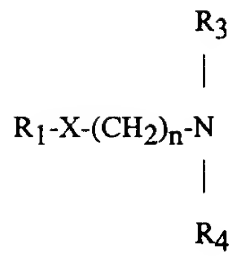
Preferred nonionic surfactants are those of the formula $R_1(OC_2H_4)_nOH$, wherein R_1 is a C_{10}-C_{16} alkyl group or a C_8-C_{12} alkyl phenyl group, and n is from 3 to about 80. Particularly preferred are condensation products of C_{12}-C_{15} alcohols with from about 5 to about 20 moles of ethylene oxide per mole of alcohol, e.g., C_{12}-C_{13} alcohol condensed with about 6.5 moles of ethylene oxide per mole of alcohol.

Additional suitable nonionic surfactants include polyhydroxy fatty acid amides of the formula:

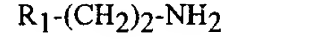


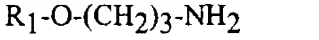
wherein R is a C_{9-17} alkyl or alkenyl, R_1 is a methyl group and Z is glycityl derived from a reduced sugar or alkoxylated derivative thereof. Examples are N-methyl N-1-deoxyglucityl cocoamide and N-methyl N-1-deoxyglucityl oleamide. Processes for making polyhydroxy fatty acid amides are known and can be found in Wilson, U.S. Patent 2,965,576 and Schwartz, U.S. Patent 2,703,798, the disclosures of which are incorporated herein by reference.

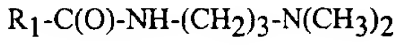
Preferred surfactants for use in the detergent compositions described herein are amine based surfactants of the general formula:

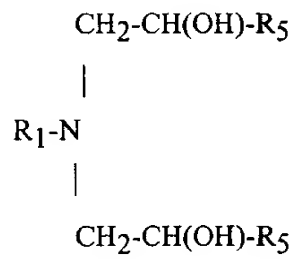


wherein R_1 is a C_6-C_{12} alkyl group; n is from about 2 to about 4, X is a bridging group which is selected from NH, CONH, COO, or O or X can be absent; and R_3 and R_4 are individually selected from H, C_1-C_4 alkyl, or (CH_2-CH_2-O(R_5)) wherein R_5 is H or methyl. Especially preferred amines based surfactants include the following:



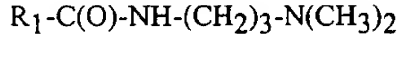






wherein R_1 is a C_6-C_{12} alkyl group and R_5 is H or CH_3. Particularly preferred amines for use in the surfactants defined above include those selected from the group consisting of octyl amine, hexyl amine, decyl amine, dodecyl amine, C_8-C_{12} bis(hydroxyethyl)amine, C_8-C_{12} bis(hydroxyisopropyl)amine, C_8-C_{12} amido-propyl dimethyl amine, or mixtures thereof.

In a highly preferred embodiment, the amine based surfactant is described by the formula:



wherein R_1 is C_8-C_{12} alkyl.

C) Detergent Builder

The detergent compositions herein may also comprise from about 0.1% to 80% by weight of a detergent builder. Preferably such compositions in liquid form will comprise from about 1% to 10% by weight of the builder component. Preferably such compositions in granular form will comprise from about 1% to 50% by weight of the builder component. Detergent builders are well known in the art and can comprise, for example, phosphate salts as well as various organic and inorganic nonphosphorus builders.

Water-soluble, nonphosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxy sulfonates. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid. Other suitable polycarboxylates for use herein are the polyacetal carboxylates described in U.S. Patent 4,144,226, issued March 13, 1979 to Crutchfield et al., and U.S. Patent 4,246,495, issued March 27, 1979 to Crutchfield et al., both of which are incorporated herein by reference. Particularly preferred polycarboxylate builders are the oxydisuccinates and the ether carboxylate builder compositions comprising a combination of tartrate monosuccinate and tartrate disuccinate described in U.S. Patent 4,663,071, Bush et al., issued May 5, 1987, the disclosure of which is incorporated herein by reference.

Examples of suitable nonphosphorus, inorganic builders include the silicates, aluminosilicates, borates and carbonates. Particularly preferred are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and silicates having a weight ratio of SiO_2 to alkali metal oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4. Also preferred are aluminosilicates including zeolites. Such materials and their use as detergent builders are more fully discussed in Corkill et al., U. S. Patent No. 4,605,509, the disclosure of which is incorporated herein by reference. Also discussed in U. S. Patent No. 4,605,509 are crystalline layered silicates which are suitable for use in the detergent compositions of this invention.

D) Optional Detergent Ingredients

In addition to the surfactants, builders and amino acid based polymer, oligomer or copolymer materials hereinbefore described, the detergent compositions of the present invention can also include any number of additional optional ingredients. These include

conventional detergent composition components such as enzymes and enzyme stabilizing agents, suds boosters or suds suppressers, anti-tarnish and anticorrosion agents, soil suspending agents, soil release agents, germicides, pH adjusting agents, non-builder alkalinity sources, chelating agents, organic and inorganic fillers, solvents, hydrotropes, optical brighteners, dyes and perfumes.

pH adjusting agents may be necessary in certain applications where the pH of the wash solution is greater than about 10.0 because the fabric integrity benefits of the defined compositions begin to diminish at a higher pH. Hence, if the wash solution is greater than about 10.0 after the addition of the amino acid based polymer, oligomer or copolymer materials of the present invention a pH adjuster should be used to reduce the pH of the washing solution to below about 10.0, preferably to a pH of below about 9.5 and most preferably below about 7.5. Suitable pH adjusters will be known to those skilled in the art.

Normally, a preferred optional ingredient for incorporation into detergent compositions is a bleaching agent, e.g., a peroxygen bleach. However, many common bleaching agents will degrade some, but not all, of the amino acid based fabric treatment materials of the present invention. Hence, before adding a bleaching agent to a detergent composition comprising an amino acid based fabric treatment material as defined herein compatibility between the bleaching agent and the amino acid based fabric treatment material must be investigated.

Another highly preferred optional ingredient in the detergent compositions herein is a detersive enzyme component. While it is known that some enzymes will degrade the peptide bonds of amino acids, the amino acid based polymer, oligomer or copolymer materials defined herein do not exhibit such degradation in the presence of enzymes. Hence, enzymes can be added to detergent compositions which comprise the amino acid based fabric treatment materials of the present invention with substantially no degradation.

Enzymes can be included in the present detergent compositions for a variety of purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains from substrates, for the prevention of refugee dye transfer in fabric laundering, and for fabric restoration. Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability, optimal thermostability, and stability to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

"Detersive enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry detergent composition. Preferred enzymes for laundry purposes include, but are not limited to, proteases, cellulases, lipases, amylases and peroxidases.

Enzymes are normally incorporated into detergent compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning-effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. Higher active levels may be desirable in highly concentrated detergent formulations.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE® and SAVINASE® from Novo and MAXATASE® from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985. See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Novo. Other preferred proteases include those of WO 9510591 A to Procter & Gamble. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583 to Novo.

Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 10. U.S. 4,435,307, Barbesgoard et al., March 6, 1984, discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase

extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander.* Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® and CELLUZYME® (Novo) are especially useful. See also WO 9117243 to Novo.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in GB 1,372,034. See also, the lipase in Japanese Patent Application 53,20487, laid open Feb. 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," or "Amano-P." Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum var. lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. LIPOLASE® enzyme derived from *Humicola lanuginosa* and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein.

The enzyme-containing compositions herein may optionally also comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detersive enzyme. Such a system may be inherently provided by other formulation actives, or be added separately, e.g., by the formulator or by a manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition.

E) Detergent Composition Preparation

The detergent compositions according to the present invention can be in liquid, paste or granular form. Such compositions can be prepared by combining the essential and optional components in the requisite concentrations in any suitable order and by any conventional means.

Granular compositions, for example, are generally made by combining base granule ingredients, e.g., surfactants, builders, water, etc., as a slurry, and spray drying the resulting slurry to a low level of residual moisture (5-12%). The remaining dry ingredients, e.g.,

granules of the essential amino acid based fabric treatment materials, can be admixed in granular powder form with the spray dried granules in a rotary mixing drum. The liquid ingredients, e.g., solutions of the essential amino acid based fabric treatment materials, enzymes, binders and perfumes, can be sprayed onto the resulting granules to form the finished detergent composition. Granular compositions according to the present invention can also be in "compact form", i.e. they may have a relatively higher density than conventional granular detergents, i.e. from 550 to 950 g/l. In such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkaline earth metal salts of sulphates and chlorides, typically sodium sulphate; "compact" detergents typically comprise not more than 10% filler salt.

Liquid detergent compositions can be prepared by admixing the essential and optional ingredients thereof in any desired order to provide compositions containing components in the requisite concentrations. Liquid compositions according to the present invention can also be in "compact form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents. Addition of the amino acid based polymer, oligomer or copolymer materials to liquid detergent or other aqueous compositions of this invention may be accomplished by simply mixing into the liquid solutions the desired amino acid based fabric treatment materials.

F) Fabric Laundering Method

The present invention also provides a method for laundering fabrics in a manner which imparts fabric appearance benefits provided by the amino acid based polymer, oligomer or copolymer materials used herein. Such a method employs contacting these fabrics with an aqueous washing solution formed from an effective amount of the detergent compositions hereinbefore described or formed from the individual components of such compositions. Contacting of fabrics with washing solution will generally occur under conditions of agitation although the compositions of the present invention may also be used to form aqueous unagitated soaking solutions for fabric cleaning and treatment. As discussed above, it is preferred that the washing solution have a pH of less than about 10.0, preferably it has a pH of about 9.5 and most preferably it has a pH of about 7.5.

Agitation is preferably provided in a washing machine for good cleaning. Washing is preferably followed by drying the wet fabric in a conventional clothes dryer. An effective

amount of a high density liquid or granular detergent composition in the aqueous wash solution in the washing machine is preferably from about 500 to about 7000 ppm, more preferably from about 1000 to about 3000 ppm.

G) Fabric Conditioning

The amino acid based polymer, oligomer or copolymer materials hereinbefore described as components of the laundry detergent compositions herein may also be used to treat and condition fabrics and textiles in the absence of the surfactant and builder components of the detergent composition embodiments of this invention. Thus, for example, a fabric conditioning composition comprising only the amino acid based fabric treatment materials themselves, or comprising an aqueous solution of the amino acid based fabric treatment materials, may be added during the rinse cycle of a conventional home laundering operation in order to impart the desired fabric appearance and integrity benefits hereinbefore described.

EXAMPLES

The following examples illustrate the compositions and methods of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

Examples I-III illustrate possible synthesis methods for compositions of the present invention, other synthesis methods will be known to those skilled in the art.

EXAMPLE I

A synthesis of a L-lysine:epsilon-caprolactam:propionic acid-polymer with molar ratios of 5:5:1 is as follows:

684 g of an 60% aqueous solution of L-lysine (365.2 g, 2.5 mol), epsilon-caprolactam (282.9 g, 2.5 mol), propionic acid (37.0 g, 0.5 mol) and sodium hypophosphite are placed in a 2 l reaction vessel equipped with an efficient stirrer and distillation head. The solution is heated under a constant stream of nitrogen to 170° C for 1 hour as water distills from the reaction. Afterwards, a water pump vacuum is applied for 1 hour to remove residual amounts of solvent and volatile products. The reddish, slightly viscous melt is cooled to 125°C and 620 g water are added slowly to result in a clear red solution. This solution is further cooled to room temperature and adjusted to a pH of approximately 7.5 with concentrated sulfuric acid (80 g) to form about a 50% stock solution. The molecular weight of the polymer is approximately 3550.

EXAMPLE II

A synthesis of a L-lysine:adipic acid-polymer with a molar ratio of 5:1 is as follows:

L-lysine monohydrate (410.5 g, 2.5 mol), adipic acid (73.1 g, 0.5 mol) sodium hypophosphite (0.1 g) and water (176 g) are placed in a 2 l reaction vessel equipped with an efficient stirrer and distillation head. The solution is heated under a constant stream of nitrogen to 152°C for 5 hours as water distills from the reaction. Following this, a water pump vacuum is applied for 1 hour to remove residual amounts of solvent and volatile products. The reddish, slightly viscous melt is cooled to 140°C and 400 g water is added slowly to result in a clear red solution after 30 min. of stirring. This solution is further cooled to room temperature and adjusted to a pH of approximately 7.5 with concentrated sulfuric acid (72 g) to form about a 50% stock solution. The molecular weight of the polymer is approximately 2160.

EXAMPLE III

A synthesis of a L-lysine:lauric acid-polymer with a molar ratio of 5:1 is as follows:

L-lysine monohydrate (365.2 g, 2.5 mol), lauric acid (100.16 g, 0.5 mol) sodium hypophosphite (0.1 g) and water (176 g) are placed in a 2 l reaction vessel equipped with an efficient stirrer and distillation head. The solution is heated under a constant stream of nitrogen to 160°C for 5 hours as water distills from the reaction. Following this, a water pump vacuum is applied for 4 hours to remove residual amounts of the solvent and volatile products. The reddish, slightly viscous melt is cooled to 140°C and 400 g water is added slowly to result in a clear red solution after 30 min. of stirring. This solution is further cooled to room temperature and adjusted to a pH of approximately 7.5 with concentrated sulfuric acid (72 g) to form about a 50% stock solution. The molecular weight of the polymer is approximately 3150.

EXAMPLE IV

Condensation product of L-lysine:aminocaproic acid and adipic acid in a molar ratio of 10:10:1

684 g of a 60% aqueous solution of L-lysine (365.2 g, 2.5 mol), aminocaproic acid (327.9 g, 2.5 mol), adipic acid (36.5 g, 0.25 mol) and sodium hypophosphite (0.1 g) are placed in a

pressurizable 2.5 l reaction vessel and blanketed with nitrogen. The reaction vessel is then sealed pressure tight and heated to 200°C for 7 h, during which time the internal pressure rises to 6.6 bar. The reaction mixture is then cooled resulting in a yellow viscous solution with a solid content of approx. 66%. 200 g of this solution is subjected to a water pump vacuum for 2 h at a temperature of 170°C to 180°C to remove solvent and volatile products. The resulting red solid is dissolved in water and adjusted to a pH of approximately 7.5 with concentrated sulfuric acid to form an approx. 48.6% stock solution.

EXAMPLE V

Condensation product of L-lysine:epsilon-caprolactam and proppionic acid in a molar ratio of 5:5:1

684 g of a 60% aqueous solution of L-lysine (365.2 g, 2.5 mol), epsilon-caprolactam (282.9 g, 2.5 mol), propionic acid (37.0 g, 0.5 mol) and sodium hypophosphite (0.1 g) are placed in a pressurizable 2.5 l reaction vessel and blanketed with nitrogen. The solution is heated to 160°C as water (317 g) is distilled from the reaction mixture. The reaction vessel is then sealed pressure tight and heated to 200°C for 4 h, during which time the internal pressure rises to 3.75 bar. The pressure is then slowly released to atmospheric pressure to remove water from the reaction mixture. Following this, a water pump vacuum is applied for 0.5 h to remove residual amounts of solvent and volatile products. The viscous melt is cooled to 125°C and 620 g water are added slowly resulting in a clear red solution, which is further cooled to ambient temperature. 600 g of this solution is adjusted to a pH of approximately 7.5 with concentrated sulfuric acid to form an approx. 53.0% stock solution. The molecular weight of the polymer is determined to be Mw=4090 g mol-1.

EXAMPLE VI

Condensation product of L-lysine:epsilon-caprolactam and C_{14}/C_{16}-alkyldiketene in a molar ration of 10:10:1

L-lysine monohydrate (821 g, 5 mol), epsilon-caprolactam (565.8 g, 5 mol) and sodium hypophosphite (0.1 g) are placed in a pressurizable 2.5 l reaction vessel and blanketed with nitrogen. The solution is heated to 192°C for approx. 1 h as water is distilled from the reaction mixture. The reaction vessel is then sealed pressure tight and heated to 200°C for 7 h, during which time the internal pressure rises to 7.25 bar. The pressure is then slowly released to atmospheric pressure to remove solvent and volatile products from the reaction mixture. Subsequently, C_{14}/C_{16}-alkyldiketene (50.4 gm 0.5 mol) is slowly added to the

reaction mixture and heating is continued for 2 h under a constant stream of nitrogen. The melt is cooled to 100°C and 1200 g water is added slowly to result in a brownish, viscous suspension which is cooled to ambient temperature. 200 g of this material is adjusted to a pH of approximately 7.5 with citric acid to form a suspension with a solid content of approx. 40.6%.

EXAMPLE VII

Granular Detergent Test Composition Preparation

Several granular detergent compositions are prepared containing various amino acid based polymer, oligomer or copolymer materials. Such granular detergent compositions all have the following basic formula:

TABLE VII

Component	Wt. %
C_{12} Linear alkyl benzene sulfonate	9
C_{14-15} alkyl sulfonate	13
Zeolite Builder	28
Sodium Carbonate	27
PEG 4000	1.6
Dispersant	2.3
C_{12-13} alkyl ethoxylate (E9)	1.5
Sodium Perborate	1.0
Soil Release Polymer	0.4
Enzymes	0.6
Amino Acid Based Fabric Treatment Materials as shown in Table IX	1.2
Perfume, Brightener, Suds Suppressor, Other Minors, Moisture, Sulfate	Balance
	100%

EXAMPLE VIII

Liquid Detergent Test Composition Preparation

Several heavy duty liquid detergent compositions are prepared containing various amino acid based polymer, oligomer or copolymer materials as described in claim 1. Such liquid detergent compositions all have the following basic formula:

TABLE VIII

Component	Wt. %
C_{12-15} alkyl ether (2.5) sulfate	19
C_{12-13} alkyl ethoxylate (9.0)	2
C_{12-14} glucose amide	3.5
Citric Acid	3
C_{12-14} Fatty Acid	2
MEA	to pH 8
Ethanol	3.4
Propanediol	6.5
Borax	2.5
Dispersant	1.2
Na Toluene Sulfonate	2.5
Amino Acid Based Fabric Treatment Materials as shown in Table IX	0.8
Dye, Perfume, Brighteners, Enzymes, Preservatives, Suds Suppressor, Other Minors, Water	Balance 100%

EXAMPLE IX

Comparative Tests

Detergent compositions comprising various lysine based polymer materials are prepared according to Tables VII and VIII above, and then evaluated for any effects caused by the various amino acid based polymers listed in Table IX. The detergent compositions are evaluated by washing samples of fabrics or garments using the test compositions, and comparing the samples to control samples laundered with compositions comprising no polymer, all other test conditions are identical.

Overall Appearance

In an Overall Appearance test, fabrics are washed using various test compositions containing either no lysine/carboxylic acid polymers (control) or one of the polmers defined in Table IX below. The fabrics are washed and after ten cycles are then comparatively graded by three judges who evaluate the overall appearance of the washed fabrics. It is the decision of the judge as to what is to be evaluated unless specific direction is given to evaluate one attribute such as color, pilling, fuzz, etc.

In the Overall Appearance test, the visual preference of the judge is expressed using the Scheff scale.

That is: 0 = No difference

1 = I **think** this one is better (unsure).

2 = I **know** this one is **a little** better.

3 = I know this one is **a lot** better.

4 = I know this one is **a whole lot** better.

For the Overall Appearance test, laundering conditions are as follows:

Washer Type: Kenmore (17 gallons)

Wash Time: 12 min

Wash Temperature: 90°F (32.2°C)

Wash Water Hardness: 6 grains per gallon

Washer Agitation: normal

Rinse Time: 2 min

Rinse Temperature: 60°F (15.6°C)

Rinse Water Hardness: 6 grains per gallon

Wash Load Fabric Content: various colored and white garments and fabrics

Wash Load Weight: 5.5 lbs (2.5 kg)

The average overall appearance test results are shown in Table IX.

TABLE IX

Lysine/carboxylic acid examples

Molecule	Fabric	FI Benefit (PSU)
Lysine/aminocaproic acid 1:1	CLOTH A Olive T-shirt	1.3 1.7
Lysine/caprolactam 1:1	CLOTH C Burgundy Flannel Green Flannel	1.5 1.2 1.3
Lysine/palmitic acid 10:1	Black socks Burgundy Flannel	1.5 1.2
Lysine/stearic acid 10:1	Black socks CLOTH B CLOTH C Burgundy flannel Green flannel	1.7 1.2 1.0 1.3 1.3

Lysine/acetic acid 10:1	CLOTH B	2.0
Lysine/acetic acid 5:1	CLOTH B CLOTH C	1.8 1.5
Lysine/aminocaproic acid/acetic acid 5:5:2	Green Flannel	1.3
Lysine/propionic acid 5:1	CLOTH C Green Flannel CLOTH B	1.3 1.0 1.7
Lysine/caprolactam/propionic acid 10:5:1	CLOTH B	1.7
Lysine/caprolactam/propionic acid 5:5:1	Black sock	1.8
Lysine/aminocaproic acid/propionic acid 5:5:2	Burgundy flannel	1.3
Lysine/lauric acid 10:1	Black sock CLOTH B CLOTH C Burgundy Flannel	2.0 1.3 2.3 1.2
Lysine/lauric acid 5:1	CLOTH B CLOTH C Burgundy Flannel	1.7 2.5 1.5
Lysine/lauric acid 4:1	CLOTH C CLOTH A	1.5 1.0
Lysine/lauric acid 3:1	CLOTH B Burgundy Flannel	1.7 1.3
Lysine/aminocaproic acid/lauric acid 5:3:1	CLOTH C	1.0
Lysine/2-ethylhexanoic acid 5:1	CLOTH B CLOTH C Green Flannel	1.2 1.5 1.7
Lysine/aminocaproic acid/2-ethylhexanoic acid 5:3:1	CLOTH B CLOTH C	2.0 2.0
Lysine/octanoic acid 5:1	Black sock CLOTH B CLOTH A CLOTH C	1.3 1.2 1.2 1.7
Lysine/adipic acid 10:1	CLOTH B CLOTH C	2.0 1.5
Lysine/adipic acid 5:1	CLOTH B CLOTH A	1.8 1.5
Lysine/aminocaproic acid/adipic acid 5:5:1	Olive T-shirt	1.1

740 CLOTH A, CLOTH B and CLOTH C indicate cotton weave fabrics that were dyed with the commercially available dyes listed below. For the tests reported in Table IX, fabrics CLOTH A, CLOTH B and CLOTH C were purchased from the Imperical Manufacturing Company, who dyed the fabrics with the following dyes:

CLOTH A = Direct Blue 1;

745 CLOTH B = Direct Black 112; and

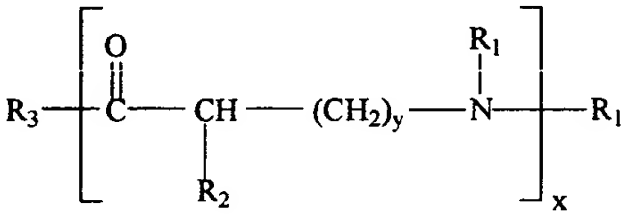
CLOTH C = Direct Violet 47.

WHAT IS CLAIMED IS:

1. A detergent composition comprising:

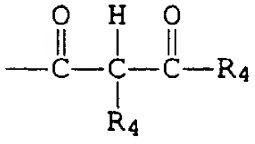
a) from 1% to 80% by weight of surfactants selected from the group consisting of nonionic, anionic, cationic, amphoteric, or zwitterionic surfactants, or mixtures thereof, and characterized in that the detergent composition further comprises;

b) from 0.1% to 10%, preferably from 0.2% to 8%, more preferably from 0.3% to 6%, and most preferably from 0.4% to 5%, by weight of a mixture of amino acid based polymers, oligomers or copolymers of the general formula:

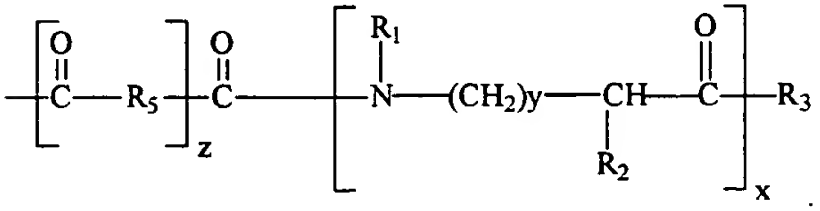


wherein the polymer, oligomer, or copolymer contains at least 5 mole %, preferably at least 10 mole %, more preferably from 20 mole %, and most preferably at least 40 mole %, of one or more basic amino acids;

each R_1 is independently selected from the group consisting of H, -C(O)-R_4, C_1-C_{18} saturated or unsaturated, branched or linear alkyl, C_2-C_{18} saturated or unsaturated, branched or linear hydroxyalkyl, C_3-C_8 cycloalkyl, C_6-C_{18} aryl, C_7-C_{18} alkylaryl, citric acid,

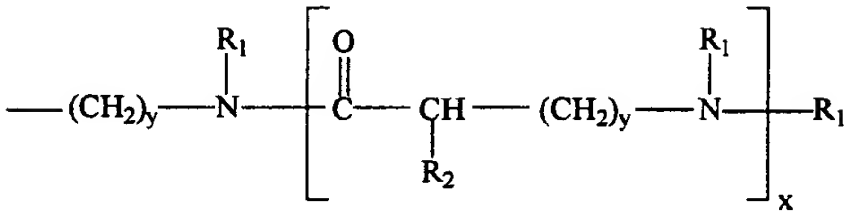


, and

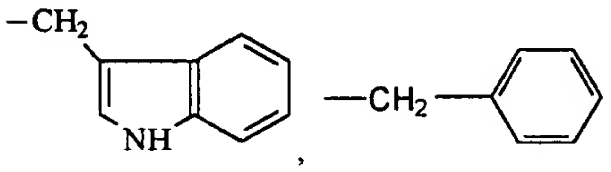


;

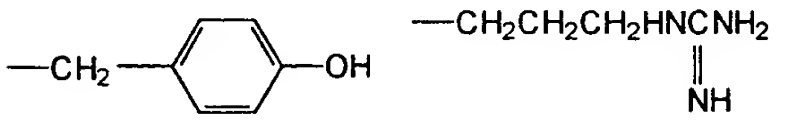
each R_2 is independently selected from the group consisting of H, NH_2,



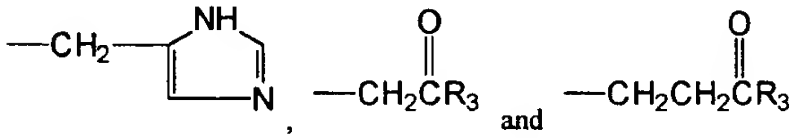
,



,



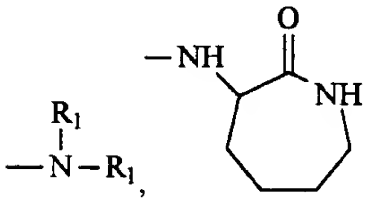
,



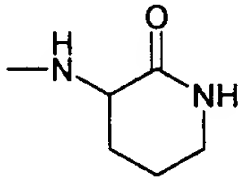
and

;

each R_3 is independently selected from the group consisting of OH, OM,



, and



;

each R_4 is independently selected from the group consisting of C_1-C_{30} saturated or unsaturated, branched or linear alkyl, C_3-C_8 cycloalkyl, C_2-C_{30} hydroxyalkyl, C_6-C_{18} aryl, C_7-C_{30} alkylaryl, and C_2-C_{100} linear or branched oxa or polyoxa-substituted alkyl;

R_5 may be absent, if R_5 is present each R_5 is independently selected from the group consisting of C_1-C_{12} linear or branched alkylene, cyclic alkylene, C_2-C_{12} linear oxa-substituted alkylene, C_2-C_{12} branched oxa-substituted alkylene, and C_3-C_{12} cyclic oxa-substituted alkylene;

wherein:

each x is independently from 0 to 200;

each y is independently from 0 to 10;

each z is independently 0 or 1; and

M is selected from compatible cations; and

provided that:

- the sum of all x's is from 2 to 200, preferably from 3 to 150, more preferably from 5 to 120, and most preferably from 5 to 100;
- any basic amine site on the polymer, oligomer, or copolymer may be optionally protonated, alkylated, or quaternized with constituents selected from the group consisting of H, CH_3, alkyl, hydroxyalkyl, benzyl and mixtures thereof;
- any amine site may be optionally alkoxylated; and
- when two R_1 groups are attached to a common nitrogen the two R_1s may form a cyclic structure selected from the group consisting of C_5-C_8 alkylene, and C_4-C_7 alkyleneoxyalkylene.

2. A detergent composition according to claim 1, wherein the amino acid based polymer, oligomer or copolymer is a condensate of lysine with at least one acid selected from the group consisting of aminocaproic acid, caprolactam, 2-ethylhexanoic acid, adipic acid, phthalic acid, terephthalic acid, oxalic acid, citric acid, C_1-C_{30} alkyldiketenes, C_1-C_{30} monocarboxylic acids that are linear or branched, saturated or unsaturated, and mixtures thereof.

3. A detergent composition according to claim 2, wherein the amino acid based polymer, oligomer or copolymer is a condensate of lysine with at least two acids selected from the group consisting of aminocaproic acid, caprolactam, 2-ethylhexanoic acid, adipic acid, phthalic acid, terephthalic acid, oxalic acid, citric acid, C_1-C_{30} alkyldiketenes, C_1-C_{30} monocarboxylic acids that are linear or branched, saturated or unsaturated, and mixtures thereof.

4. A detergent composition according to claim 2, wherein the lysine and the acid are condensed at a ratio of lysine:acid of from 1:1 to 10:1.

5. A detergent composition comprising:

a) from 1% to 80% by weight of surfactants selected from the group consisting of nonionic, anionic, cationic, amphoteric, or zwitterionic surfactants, or mixtures thereof, and characterized in that the detergent composition further comprises;

b) from 0.1% to 10%, preferably from 0.2% to 8%, more preferably from 0.3% to 6%, and most preferably from 0.4% to 5%, by weight of a mixture of amino acid based polymers which are obtainable by condensing at a temperature of at least 120°C:

(i) a basic amino acid selected from the group consisting of lysine, arginine, ornithine, tryptophane and mixtures thereof;

(ii) a copolymerizable compound selected from the group consisting of saturated monobasic carboxylic acids, unsaturated monobasic carboxylic acids, polybasic carboxylic acids, carboxylic acid anhydrides, diketenes, monohydroxycarboxylic acids, monobasic polyhydroxycarboxylic acids and mixtures thereof; and

(iii) optionally, at least one compound selected from the group consisting of amines, lactams, nonproteinogenic acids, alcohols, alkoxylated amines, amino sugars, carbohydrates, sugar carboxylic acids and mixtures thereof; and

wherein compounds (i) and (ii) are present in a molar ratio of (i):(ii) of from 100:1 to 1:1.

6. The detergent composition according to claim 5, wherein the molar ratio of basic amino acid (i) to copolymerizable compound (ii) is of from 100:1 to 2:1, preferably from 50:1 to 2:1, and more preferably 20:1 to 5:1.

7. The detergent composition according to claim 5, wherein the molar ratio of (i):(iii) is from 100:1 to 1:20.

8. The detergent composition according to claim 5, wherein the amino acid based polymers are obtained by condensing:

(i) lysine; and

(ii) at least one compound selected from the group consisting of palmitic acid, stearic acid, lauric acid, octanoic acid, propionic acid, acetic acid, 2-ethylhexanoic acid, adipic acid, succinic acid, citric acid and mixtures thereof.

9. The detergent composition according to claim 5, wherein the amino acid based polymers are obtained by condensing:

(i) a basic amino acid selected from the group consisting of lysine, arginine, ornithine, tryptophane and mixtures thereof;

(ii) at least one compound selected from the group consisting of saturated carboxylic acids, unsaturated carboxylic acids, polybasic carboxylic acids, carboxylic acid anhydrides, hydroxycarbxoylic acids, monobasic polyhydroxycarboxylic acids and mixtures thereof; and

(iii) at least one compound selected from the group consisting of amines, lactams having 5 to 13 atoms in the ring, non-proteinogenic aminocarbxoylic acids, alcohols, alkoxylated amines, amino sugars, carbohydrates, sugar carboxylic acids and mixtures thereof; and

wherein compounds (i):(ii) are present in a molar ratio of (i):(ii) of from 100:1 to 2:1 and wherein compounds (i):(iii) are present in a molar ratio of (i):(iii) of from 20:1 to 1:20.

10. The detergent composition according to claim 5, wherein the amino acid based polymers are obtained by condensing:

(i) a basic amino acid selected from the group consisting of lysine, arginine, ornithine, tryptophane, and mixtures thereof;

(ii) at least one alkyldiketene having 1 to 30 carbon atoms in the alkyl group; and

(iii) optionally, at least one compound selected from the group consisting of amines, lactams, nonproteinogenic amino acids, alcohols, alkoxylated amines, amino sugars, carbohydrates, sugar carboxylic acid, and mixtures thereof.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/37

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 09638 A (UNILEVER PLC ;UNILEVER NV (NL)) 13 April 1995 see claims 1,5,6,8-13 see examples; tables ---	1
X	US 5 540 863 A (WOOD LOUIS L ET AL) 30 July 1996 see claims 1,8,10,22; table 2 ---	1
A	WO 94 01486 A (BASF AG ;KRONER MATTHIAS (DE); HARTMANN HEINRICH (DE); BOECKH DIET) 20 January 1994 see polycodensate 4 see claims 1,2,5; example 27 see page 18, line 35 - page 19, line 34 see page 26, line 23 --- -/--	1,2,4-8

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 November 1998	02/12/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Loiselet-Taisne, S

1

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 028 689 A (HEINZ HANS-DETLEF ET AL) 2 July 1991 see claims; examples 1,16,23	1-9
A	EP 0 454 126 A (MONTEDIPE SRL) 30 October 1991 see claim 1; examples 11,12	1
A	WO 94 24254 A (BASF AG ;KRONER MATTHIAS (DE); SCHORNICK GUNNAR (DE); BAUR RICHARD) 27 October 1994 see page 3, line 16 - line 22; claim 1	1
A	US 5 639 723 A (KRONER MATTHIAS ET AL) 17 June 1997 see column 5, line 62; claims 1,5	1
X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 011, 28 November 1997 & JP 09 176689 A (T PAUL KK), 8 July 1997 see abstract	1,10
X	PATENT ABSTRACTS OF JAPAN vol. 095, no. 009, 31 October 1995 & JP 07 166200 A (MITSUBISHI MATERIALS CORP), 27 June 1995 see abstract	1,10
X	DATABASE WPI Section Ch, Week 9444 Derwent Publications Ltd., London, GB; Class D22, AN 94-354977 XP002084052 & JP 06 279791 A (MITSUBISHI MATERIALS CORP), 4 October 1994 see abstract	1,10

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9509638 A	13-04-1995	AU 695290 B	13-08-1998
		AU 7810694 A	01-05-1995
		BR 9407770 A	18-03-1997
		CA 2169084 A	13-04-1995
		EP 0722327 A	24-07-1996
		HU 74379 A	30-12-1996
		JP 9503216 T	31-03-1997
		US 5629282 A	13-05-1997
		ZA 9407788 A	09-04-1996
US 5540863 A	30-07-1996	US 5389303 A	14-02-1995
		AU 7723294 A	27-03-1995
		CA 2171328 A	16-03-1995
		EP 0719317 A	03-07-1996
		JP 9504313 T	28-04-1997
		NO 960885 A	05-03-1996
		WO 9507329 A	16-03-1995
WO 9401486 A	20-01-1994	DE 4221875 A	05-01-1994
		DE 59307218 D	02-10-1997
		EP 0648241 A	19-04-1995
		ES 2105287 T	16-10-1997
		US 5747635 A	05-05-1998
US 5028689 A	02-07-1991	DE 3831709 A	29-03-1990
		EP 0360060 A	28-03-1990
		JP 2115225 A	27-04-1990
EP 0454126 A	30-10-1991	IT 1240684 B	17-12-1993
		US 5658872 A	19-08-1997
		US 5328631 A	12-07-1994
WO 9424254 A	27-10-1994	DE 4311854 A	13-10-1994
		DE 59406092 D	02-07-1998
		EP 0693117 A	24-01-1996
		US 5665693 A	09-09-1997
US 5639723 A	17-06-1997	DE 4225620 A	10-02-1994
		WO 9403576 A	17-02-1994
		EP 0652936 A	17-05-1995